LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR -89-2685

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG 36

TITLE NON-AQUEOUS POLYPYRROLE COLLOIDS: SYNTHESIS AND CHARACTERIZATION

LA-UR--89-2685

DE89 016589

AUTHOR(S) Steven P. Armes and Mahmoud Aldissi

SUBMITTED TO Proceedings of the 21st Europhysics Conference on Macromolecular Physics, organized in Lodz, Poland, September 4-8, 1989, to be published as a full paper in Synthetic Metals

DISCLAIMER

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

NON-AQUEOUS POLYPYRROLE COLLOIDS: SYNTHESIS AND CHARACTERIZATION

S. P. Armes[a] and M. Aldissi
Materials Science and Technology Division, Los Alamos National Laboratory, P. O. Box 1663, Los Alamos, NM 87545, USA

ABSTRACT

The preparation of sterically-stabilized polypyrrole colloids via a dispersion polymerization route in non-aqueous media is described for the first time. Pyrrole polymerization was achieved using $FeCl_3$ as an oxidant/dopant in organic solvents such as methyl acetate, methyl formate and propyl formate. Macroscopic precipitation was prevented by the use of poly (vinyl acetate) as a polymeric surfactant. Other surfactants, used successfully in aqueous media, were incompatible and consequently resulted in precipitation of polypyrrole. Several techniques were used for characterization of the dispersions including transmission and scanning electron microscopies (TEM and SEM), thermogravimetric analysis (TGA), velocity charge analysis and visible absorption spectroscopy. TEM indicated a polydisperse spherical morphology with a particle diameter in the range 100-300 nm. The compressed pellet conductivity of the dried dispersion was 0.1 S/cm. These dispersions are often compared with aqueous bulk polypyrrole and aqueous dispersions.

a Current address is School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

INTRODUCTION

In the past few years there have been several publications on the preparation of colloidal polypyrrole particles in aqueous media via a dispersion polymerization route [1-6]. In this approach, the pyrrole monomer is added to a stirred solution containing $FeCl_3$ oxidant and a suitable polymeric surfactant such methyl cellulose, poly (vinyl alcohol-co-acetate), poly (vinyl pyrrolidone) and poly (vinyl pyridine). The surfactant adsorbs onto the growing polypyrrole chain/particle and prevents further aggregation by a steric stabilization mechanism. Such systems improve the processability of the normally intractable electroactive component. Recently, a method by which polypyrrole particles prepared in aqueous media and later transferred into non-aqueous media has been described [6]. The present work describes the preparation of colloidal polypyrrole directly in non-aqueous media.

Initially, several potential advantages were the reason for carrying out this study, particularly, due to the fact that bulk polypyrrole powder prepared using $FeCl_3$ oxidant in certain organic solvents such as ethyl acetate exhibits higher conductivity and air-stability than the ones prepared in aqueous media [7,8]. This is probably due to the incorporation of $FeCl_4^-$ rather than only Cl^- dopant anions into the polypyrrole backbone. The highest conductivities for bulk polypyrrole using $FeCl_3$ oxidant in organic media are obtained if the oxidant/monomer ratio is higher than 2.0 [7]. This criterion has been shown to be unnecessary for polymerization in aqueous media [9].

As far as the authors are concerned, only diethylether, dioxan, methanol and various esters permit the preparation of polypyrrole having a conductivity higher than the unity. Of these solvents, diethyl ether does not dissolve many would-be polymeric surfactants [10], while methanol requires very high oxidant concentrations for useful yields [8,11].

Our initial experiments using esters such as ethyl acetate or pentyl acetate or solvent mixtures failed to produce stable dispersions and resulted in macroscopic precipitation. However, we found that the use of the more polar methyl acetate, methyl formate or propyl formate allowed the preparation of stable colloidal dispersions of sub-micronic polypyrrole particles.

The preparation of these dispersions was initially attempted using various polymeric surfactants that appeared to be good candidates for the steric stabilization of polypyrrole particles. Of these surfactants, hydroxypropyl cellulose, poly (n-propyl methacrylate) and poly (vinyl alcohol-co-acetate) (20/80) yielded an insoluble complex before adding the monomer. Cellulose nitrate, poly (butyl methacrylate), poly (2-ethyl hexyl acrylate) and poly (hexadecyl methacrylate) were not efficient steric stabilizers and resulted in precipitation of polypyrrole particles. We found, however, that use of poly (vinyl acetate), referred to as PVAc, resulted in the formation of colloidal dispersions of polypyrrole.

EXPERIMENTAL

Materials Synthesis:

In a typical experiment 1 ml of pyrrole was injected into a stirred solution containing 5.47g of $FeCl_3$ and 1.0 g of PVAc, whose molecular weight M_w is 266,300 and polydispersity is 3.0, in 100 ml of methyl acetate and the

polymerization allowed to proceed for 15h. at 25° C. The resulting black colloidal dispersion was centrifuged at 5,000 rpm for 40 min. to produce a black sediment and a dark supernatant. The supernatant was discarded and the sediment washed several times with 2-3 ml of methyl acetate. The sediment was then redispersed in methyl acetate by mechanical agitation and ultrasonics. The dispersion was vacuum-filtered to remove traces of precipitate.

Materials Characterization:

Conductivity measurements were performed using the four-probe technique on compressed pellets of the freeze-dried dispersions. SEM studies were made on compressed pellets of the dried dispersion, coated with gold, using a CAMSCAN series 4 instrument. TEM studies were made on dilute dispersions dried down on carbon-coated copper grids using a Phillips EM 400 instrument. An average particle size was estimated by counting at least 100 particles using a DAPPLE image analyzer. Furthermore, more precise particle size determination was done using Charge Velocity Analysis technique. Visible absorption spectra of dilute dispersions were recorded on a DU-7 Beckman spectrophotometer. Microanalyses were determined by Galbraith Laboratories. Thermogravimetric Analysis was performed using a Perkin Elmer TGS-2 Instrument.

RESULTS AND DISCUSSION

Electron microscopy (TEM and SEM) studies on the dried-down dispersions indicate in all cases a polydisperse spherical morphology with a particle diameter in the range 100-300 nm. In Fig. 1 are shown scanning electron micrographs of polypyrrole dispersions and of bulk polypyrrole, both prepared in methyl acetate, for comparison. The micrographs illustrate the typical spherical morphology of the particles whose diameter is independent of the solvent used in the oxidative polymerization process. When compared to the bulk polymer, polypyrrole colloidal particles are less than half the size of the former. This result is similar to the one obtained for the aqueous bulk and colloidal dispersions of polypyrrole. The bulk polymer tends to aggregate in larger particles in the form of large globules or fibrils. This is probably due to an increased interchain interaction compared to its colloidal counterpart in which the polymeric surfactant chains act as a limiting factor for such an interaction. At the moment we do not have an exact explanation as to why the particles have a wide polydispersity. A more precise determination of the particle size using charge velocity analysis technique of the accelerated particles has shown (Fig. 2) a trimodal distribution with an average particle diameter of 225 $\pm$ 75 nm obtained for the dispersions prepared in 200 ml methyl acetate in the presence of 1.0 g PVAc, 5.47 g $FeCl_3$ and 1.0 ml pyrrole. Such a measurement gave an average particle diameter for colloids prepared in methyl acetate, methyl formate and propyl formate in the same experimental conditions of 253 $\pm$ 107 nm, 276 $\pm$ 90 nm and 259 $\pm$ 82 nm respectively.

The microanalytical data obtained for dispersions prepared in methyl acetate and methyl formate and those of the bulk polymer add up to more than 99% with an oxygen ratio of approximately 10%. This high oxygen content can be attributed to the presence of trapped solvent molecules and to the oxidation of polypyrrole during polymerization. The chlorine/iron mole ratios for bulk polymer prepared in methyl acetate and the colloids prepared in methyl acetate and methyl formate under the same conditions are 3.9, 4.2 and 4.6 respectively. Furthermore, Mossbauer spectroscopy measurements has shown that the predominant (> 95%) oxidation state

of iron is +2. Therefor, we may assign the iron compound incorporated as the dopant anion to be $FeCl_4^{2-}$ or a mixture of the latter with Cl^- anions. However, additional washing of the dispersions or the bulk polymer with methanol yield a composition with very little iron (<1%), with no effect on the conductivity. This result indicates that doping is attributed mostly to Cl^- anions and that iron does not play a major role in the doping process.

Regardless of the iron content, room temperature conductivities measured using the four-probe technique on pellets of the dried-down dispersions vary with the type and volume of solvent and the initial amount of the polymeric surfactant PVAc under similar experimental conditions (polymerization temperature and amount of oxidant). The results are shown in table 1.

TABLE 1: Conductivity of Non-Aqueous Polypyrrole Colloids

Solvent	Solvent Volume (ml)	Weight of PVAc (g)	Conductivity S/cm
methyl acetate	100	1.0	1.1 x 10-1
methyl acetate	200	1.0	4.5 x 10-3
methyl acetate	200	2.00	8.0 x 10-4
methyl formate	100	1.0	6.0 x 10-2
methyl formate	200	1.0	1.4 x 10-3
propyl formate	200	1.0	3.7 x 10-6
propyl formate	200	2.0	7.5 x 10-6

As indicated in table 1, the conductivity decreases when the initial amount of surfactant is increased for a given amount and a given type of solvent. This is due to an increased amount of the physically adsorbed PVAc which is an insulating material. Additionally, dilution of the reaction components results in a decrease of conductivity regardless of the polymerization time. A probable explanation for this observation is that the polymeric surfactant chains are physically adsorbed on polypyrrole particles at a faster rate and therefore in larger relative amounts. It is important to note that the rate of polypyrrole formation is lowered upon dilution. Among the solvents used in this oxidative polymerization, the smaller alkyl radicals associated with a more polar character of the solvent give better conductivities. For comparison, the conductivity of bulk polypyrrole prepared in methyl acetate measures 0.23 S/cm, which is in the same range as that of its colloidal counterpart.

Room temperature conductivity of the first example in table 1 which gave a conductivity of 0.11 S/cm was monitored upon exposure to air. The conductivity measured after 3 months was 0.067 S/cm, 0.058 S/cm after 6.5 months and 0.039 S/cm after 9 months. Such a trend in variation of conductivity upon exposure to

air is similar to polypyrrole colloids prepared in aqueous media and to the bulk polymer prepared in aqueous or non-aqueous media using $FeCl_3$ as the oxidant.

The maximum absorption observed in the optical spectra of the various colloids is in the range 460-480 nm depending on the polymerization solvent. This is typical for polypyrrole synthesized using the various techniques and reaction media. Because optical absorption is an intrinsic property of the conjugated chain, optical absorption characteristics of the colloidal dispersions suggest that the average length of the conjugated segments of polypyrrole chains is basically unperturbed by their synthesis in the form of a colloid. The same conclusion can be made for polypyrrole colloids synthesized in aqueous media. Therefore, the lower conductivity measured for the non-aqueous colloids compared to their aqueous counterparts or the bulk polymer is due to the nature of the solvent and its role in the polymerization process.

Thermogravimetric analysis (TGA) was done on the colloids prepared in the various solvents. Thermograms of the colloids prepared in methyl acetate and methyl formate and that of the aqueous polypyrrole colloid prepared in the presence of poly (vinyl alcohol-co-acetate) are shown in Fig. 3 to illustrate the thermal stability of the materials. Although there are different transitions in the thermal degradation of the non-aqueous colloids, the overall behavior is similar in that the weight loss is comparable at the same temperatures. The weight loss in the case of the aqueous colloid follows a similar trend, but with a smoother curve, to that of the non-aqueous ones. In all cases thermal degradation starts above 60°C. This process, when it involves weight loss, is usually accompanied by a decrease in conductivity of conducting polymers in general.

CONCLUSIONS

We have demonstrated for the first time that colloidal dispersions of polypyrrole can be synthesized in organic solvents that have a sufficient polarity to dissolve the appropriate polymeric surfactant. However, lower conductivities than for the aqueous colloids are obtained. This shows that the solvent plays an important role in the polymerization process. The polydisperse spherical morphology could also be due to the solvent since the same behavior is not observed in aqueous media. Furthermore, non of these colloids are film-forming. The oxidant used in the polymerization process must be compatible with the polymeric surfactant. Because of this compatibility, only PVAc was found to yield stable dispersions of polypyrrole. For the same reason, only $FeCl_3$ could be used as an oxidant. An attempt to use $Cu(ClC_4)_2$. $6H_2O$ in acetonitrile in the presence of PVAc at or below room temperature failed and resulted in the precipitation of polypyrrole due to the high rate of reaction.

REFERENCES

1. R. B. Bjorklund and B. Liedberg, J. Chem. Soc., Chem. Commun., 1293 (1986).

2. S. P. Armes and B. Vincent, J. Chem. Soc., Chem. Commun., 288 (1987).

3. S. P. Armes, J. F. Miller and B. Vincent, J. Coll. Inter. Sci., 118, 410 (1987).

4. S. P. Armes, M. Aldissi and S. F. Agnew, Synth. Met., 28, C837 (1989).

5. S. P. Armes, Ph.D. thesis, University of Bristol, UK (1987).

6. N. Cawdery, T. M. Obey and B. Vincent, J. Chem. Soc., Chem. Commun., 1189 (1988).

7. R. E. Myers, J. Elect. Mat., 2, 61 (1986).

8. S. P. Armes, unpublished results.

9. S. P. Armes, Synth. Met., 20(3), 367 (1987).

10. J. A. Walker, L. F. Warren and E. F. Witucki, ACS Polym. Prepr., 28(2), 256 (1987).

11. B. Vincent, private communication.

ACKNOWLEDGMENTS

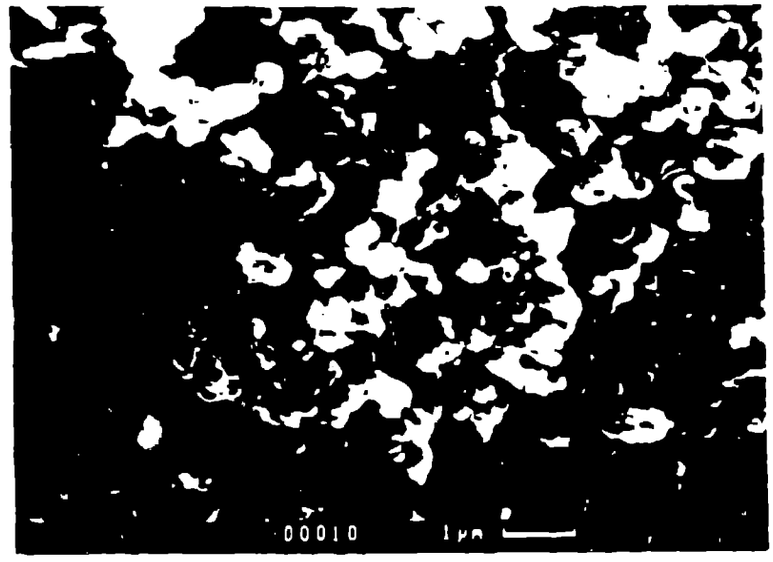
The authors want to thank R. Sebring for assistance with the TEM, J. F. Smith with the SEM, P. W. Keaton and coworkers with the charge velocity analysis and R. D. Taylor with the Mossbauer spectroscopy. This work was supported by the DOE Office of Basic Energy Sciences.

FIGURE CAPTIONS

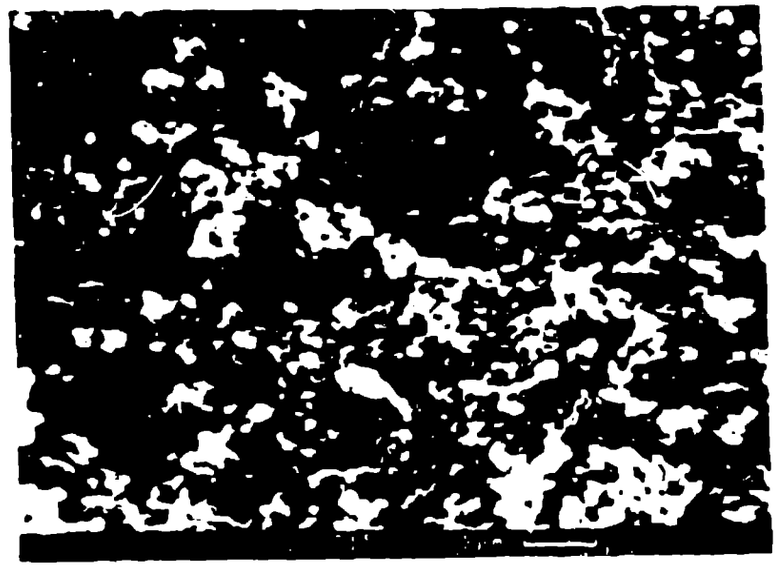
Fig. 1 Scanning electron micrographs of (a) bulk polypyrrole and (b) polypyrrole colloid, both prepared in methyl acetate.

Fig. 2 Particle radius distribution of colloidal polypyrrole prepared in methyl acetate determined by charge velocity analysis technique.

Fig. 3 Thermogravimetric analysis of colloidal polypyrrole prepared in (a) methyl formate, (b) methyl acetate and (c) water.



(a)



(b)

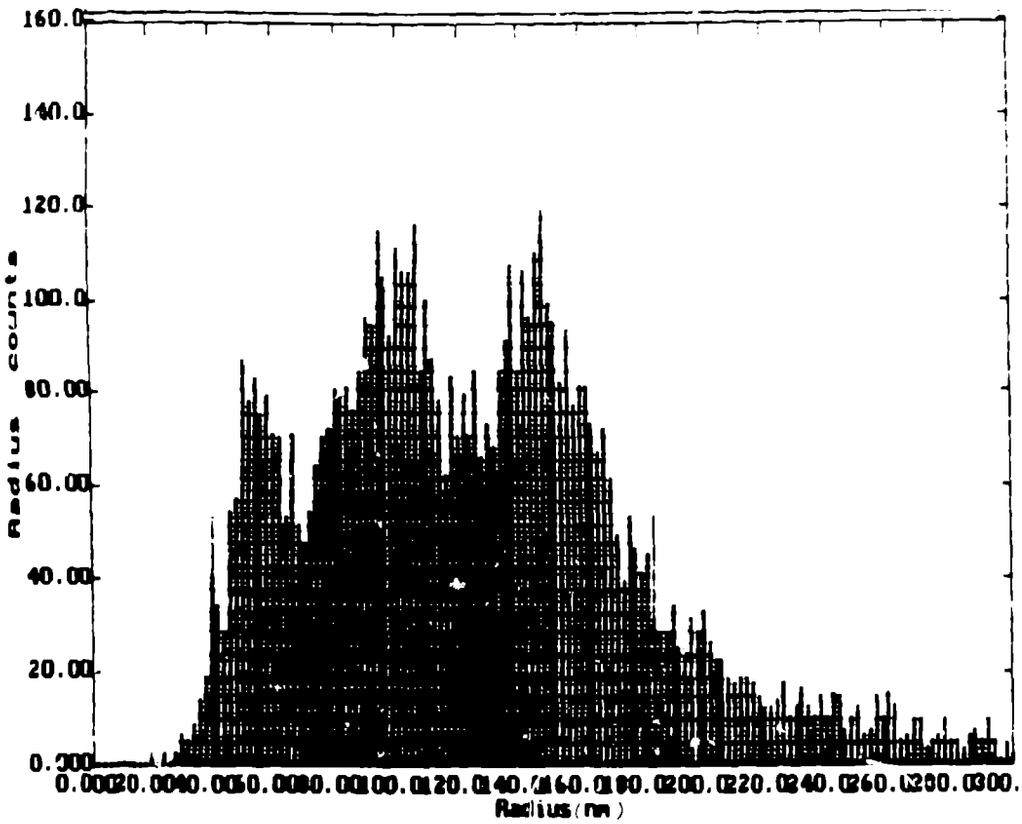
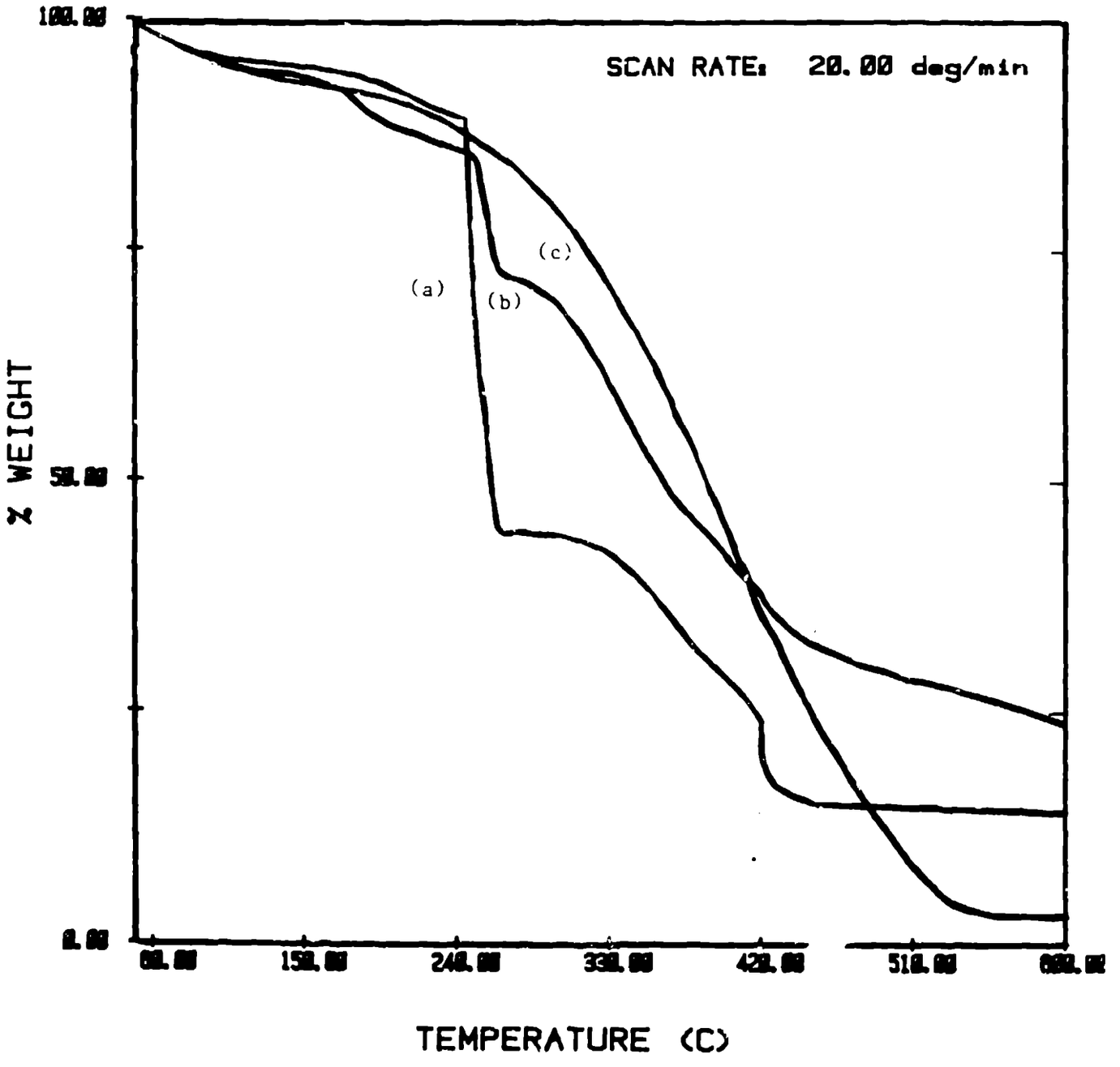

160.0
140.0
120.0
100.0
80.00
60.00
40.00
20.00
0.200
Radius counts
0.000
Radius (nm)

Fig. 2


SCAN RATE: 20.00 deg/min
(a)
(b)
(c)
% WEIGHT
TEMPERATURE (C)